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THE CASE AGAINST MERCURY

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ENVIRONMENTAL PROTECTION AGENCY
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ABSTRACT

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The toxicity of mercury is increased more than tenfold when it is converted to methyl mercury which destroys nerves in the brain and advances senility. Bacteria convert mercury in aquatic sediments into methyl mercury which is concentrated by predatory fish.

THE CASE AGAINST MERCURY *

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Robert B. Dean **

Mercury sprung into our headlines less than two years ago when fish in Lake St. Clair above Detroit were shown to contain hazardous levels of methyl mercury. This discovery destroyed a fishery and drew attention to a problem that had been simmering on the back burner for a long time. Looking at what was known about the mercury problem before those fish were analyzed one wonders why the anonymous "they" didn't do something earlier. Rather than cast stones backward in time let us look at the evidence. Most of the available evidence which led to the setting of guidelines on mercury is reviewed in the publication "Hazards of Mercury," a special report to the Secretary of HEW. The chairman of the special interdepartmental committee that wrote this report was Dr. Norton Nelson, Director of the Institute of Environmental Medicine, New York University. I shall refer to this review as the Nelson Report (see references at the end of this paper).

Inorganic mercury is a poison. Known to the alchemists as corrosive sublimate, mercuric chloride was a common suicide chemical before barbiturates became popular (Montagues, p. 18). The cumulative toxic effects of mercury vapors and dusts were well known. Nevertheless, mercury metal was generally considered safe and inorganic mercury compounds were used widely by doctors for everything from sterilizing instruments to cathartics. It is true that you can swallow a spoonful of mercury and probably suffer no ill effects because the liquid metal goes through you so fast. However, constant

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exposure to the vapors from that same spoonful can produce chronic mercury poisoning. The Maximum Allowable Concentration (MAC) of mercury vapor in air is 0.1 mg per cubic meter of air (Friberg). When I was at Professor August Krogh's laboratory in Copenhagen before the war, symptoms of mercury poisoning appeared in scientists who had been working in a pressure chamber. The vapors from small globules of mercury spilled on the floor were being recirculated through the chamber, providing the prolonged exposure necessary to cause poisoning.

With regard to chronic exposure, mercury metal can be lumped with inorganic mercury compounds because it is easily oxidized, especially by sulfur compounds. As already stated, even minute quantities of the vapor are toxic. Mercury ions bind to sulfhydryl groups of proteins destroying cells. The sulfur-containing amino acid, cystine, can form a low molecular weight compound with mercury that can circulate in the body and carry mercury to other cells (Norseth and Clarkson). The ultimate target cells are principally nerve cells and most of the clinical symptoms of mercury poisoning are those of nerve damage. According to the Merck Index, some of these symptoms are: "muscle tremors, jerky gait, spasms of extremities, personality changes, depression, irritability, nervousness." These symptoms arise from long exposure to low concentrations of mercury. They resemble symptoms of senility right down the line and for good reason: senility results from loss of nerves in the brain and body--not enough to terminate life but enough to take the fun out of living.

One special group of mercury compounds is ten or more times as poisonous as inorganic mercury. These are the alkyl mercuries. The prototype is methyl mercury cation, CH_3Hg^+ . Its salts are volatile, the chloride

evaporates at 100° C. Dimethyl mercury is oil soluble and behaves like octane. Under acid conditions and to some extent in the body it can be converted back to monomethyl compounds. Methyl mercury cation, like inorganic mercury cations, forms compounds with sulfhydryl groups on proteins. The difference comes from the volatility and oil solubility of methyl mercury compounds which enables them to penetrate the blood-brain barrier and concentrate in the nerve cells of the brain. Methyl mercury attacks the higher levels of the brain, leading to loss of eyesight, hearing and speech (Löffroth). The intellect progressively deteriorates while the vital functions are preserved.

Methyl mercury has been useful as a fungicide for seeds. The compound has resulted in better crops and may have saved more human lives from starvation than it has taken when misused. Of course, there have been many cases of misuse. No doubt the most dramatic case in the United States was when pork from pigs fed on treated seed grain poisoned the Huckleby family in Alamogordo. You may have seen them on TV. The Montagues vividly retell this story in their pocket book, "Mercury."

Ten or more years ago the Swedes began to collect evidence that birds were suffering from methyl mercury poisoning (Ackefors). Significantly eagles and hawks had more methyl mercury than smaller birds which were feeding on treated seed grain. This fact pointed to the insidious nature of methyl mercury--its concentration at the top of the food chain. Such concentration can only occur if the substance is bound to body organs and slowly excreted. It is significant that the Huckleby hogs had about as much methyl mercury (28 ppm) as the treated seed (32 ppm) although they

ate other things besides the treated grain (Nelson Report, p. 10). The results of using methyl mercury compounds in agriculture extend so far beyond protecting seeds from fungal attack that many countries beginning with Sweden have banned the use of alkyl mercurials in seed treatment and a similar ban is in effect in this country.

At about the same time mercury was found in Swedish fish (Ackefors). Of course fish don't eat seed grain, and the obvious source of mercury was discharges of mercurial slimicides, especially phenyl mercury compounds from paper mills. Our country had been phasing out such slimicides for paper production because of potential contamination of food packages, but mercury compounds are in common use for mildew control in paints and other applications. Careful analyses have shown that nearly all the mercury in fresh water fish was in the form of methyl mercury, not inorganic or phenyl mercury (Westöö, Nelson Report). How could phenyl mercury be converted to methyl mercury? Methyl mercury in sea foods had already poisoned many people in Japan during the Minamata Bay disaster and also at Niigata. At Minamata a chemical factory discharged both inorganic and methyl mercury (Nelson Report). In Sweden it was harder to account for the methyl compound in fish. Certainly agricultural runoff was insufficient. The answer lay in bacterial conversion.

Bacteria, like all living cells, can be poisoned by mercury. At one time surgeons disinfected their hands with a 500 ppm solution of bichloride of mercury before operating (Merck Index). Mercury, of course, occurs in nature, and some bacteria have learned to accommodate themselves to low levels of mercury which kill off their competitors. One way they do this is to convert the mercury to a volatile substance which will escape.

Conversion to inorganic mercury vapor and conversion to methyl mercury compounds are both possible (Magos et al). Jensen and Jernelöv in Sweden and others since then used fish as collectors, and showed that mercury compounds can be converted into methyl mercury by bacteria in organic mud at the bottom of an aquarium. Bacteria have no nerve cells and are therefore much less sensitive than animals to methyl mercury poisoning. They also absorb all their food from solution and run no danger of swallowing food containing methyl mercury. So detoxification by methylation serves the bacteria cell even though the results may spell trouble for fish eaters.

Studies in Japan, Sweden, and in this country have indicated that all forms of mercury can be converted to the element and on to methyl mercury by bacterial action (Furukawa et al, Jensen and Jernelöv, Wood et al). Conversion of metallic mercury to mercuric ion does not require bacterial intervention. Even mercuric sulfide, the most insoluble form of mercury, can be converted to methyl mercury under aerobic conditions (Fagerström and Jernelöv). These findings completely reversed common knowledge about the chemistry of mercury in nature. Formerly we argued that mercury metal is heavy and will sink to the bottom of sediments where it will be buried. If any chemical conversion occurs, it would be to mercury sulfide, a compound insoluble even in strong nitric acid. Mercury compounds would bind to organic matter in sediments where their toxicity should effectively prevent further biological conversion. Only a very few chemists had studied methyl mercury, the few textbooks that mention the compound comment on its toxicity and go on to discuss the peculiar chemistry of the carbon-mercury bond (Whitmore).

The average chemist, based on his training, could see no special hazard in discharges of mercury. The chemical engineer could demonstrate that it was more economical to buy make-up mercury than to attempt to recover normal losses. In the case of chloralkali plants, these losses were as much as half a pound of mercury per ton of caustic soda. The consumption of mercury in the chloralkali industry was over one and a half million pounds in 1969 and a large part of that reached the nearest waterway. When the fish in Lake St. Clair were found to contain high levels of mercury, it was easy to find the lost mercury in the mud at the bottom of the St. Clair River below a chemical factory (Dunlap).

It is to the credit of the chemical engineering profession that discharges of mercury in wastewater from many chloralkali plants were reduced by ninety percent or more within a few weeks. This was possible because the needed technology had been summarized by workers in Sweden. A paper telling how to reduce mercury discharges was presented at the Purdue Industrial Waste Conference in May 1969 but was not published for nearly two years (Bouveng and Ullman). However, copies were privately circulated in the industry. The Swedish paper showed that "a considerable reduction of the 'normal' losses of mercury may be achieved at a cost which seems to be easily covered by savings on costs for replenishment" but few chloralkali plants made any attempt to reduce discharges before the Lake St. Clair incident.

Another problem is analytical. The standard methods for heavy metals depend upon ashing as a preliminary step to destroy organic matter. Unfortunately, ashing drives off mercury as the vapor. Once I was told

that there was no mercury in coal. The analyses showing zero mercury had all been run on coal ash. More recent analyses run from 0.2 to 33 ppm mercury, depending on the source (Joensuu). One coal gasification plant in England found mercury metal in its condenser coils (Holdsworth). In Sweden a lot of work was done by neutron activation of whole samples followed by radioactive assay (Nelson Report, p. 55). Not everyone interested in mercury has access to neutron activation and the method is costly and time-consuming at the best.

Recently a number of devices based on atomic absorption of the light from mercury vapor lamps have appeared. If mercury in a sample can be converted to the metal, it is now possible to determine mercury down to concentrations below 0.1 ppb (1 in 10^{10}). A relatively simple technique is available for samples such as flesh which can be decomposed in cold acid without loss of volatile mercury compounds (Hatch and Ott). More refractory wastes such as oils, soils and coal are harder to prepare for analysis.

The Environmental Protection Agency has been concerned with mercury pollution, through its component organizations for many years. Research is going on at EPA's National Environmental Research Center, Cincinnati, to develop better methods for determining the presence and quantity of mercury in the environment and the fate of mercury in various sewage treatments.

The determination of methyl mercury salts is more difficult. These volatile substances must be extracted, cleaned up and determined by gas chromatography (Newsome). Very few laboratories are capable of making

reliable analyses for methyl mercury whereas any analytical chemist who can invest a few hundred dollars in a mercury meter can run analyses for total mercury. As a result, although methyl mercury is the real culprit in foods, the vast majority of analyses that you will see are based on the total mercury content. We do know that fresh water fish and birds concentrate methyl mercury (Löfroth) and it is a safe assumption, until proved otherwise, that mercury in foods is in its worst form, that is as methyl mercury.

As you probably know, legal action has been taken against several companies for what EPA Administrator William D. Ruckelshaus has called "the serious problem of mercury pollution." The Nelson Report reviews the studies that led to the setting of a guideline at 0.5 part per million of mercury in fish. The margin of safety is believed to be too close to the danger level by many (Löfroth, p. 19). If it were set much lower, most fish would be banned; if it were set much higher, the levels would be no less than those that have caused serious poisoning in the past. The evidence which suggests that methyl mercury can cause genetic damage which may lead to birth defects is also reviewed in the Nelson Report. Much more work needs to be done in this area and I will rest my case on the demonstrated nerve damage.

Remember that methyl mercury causes permanent loss of nerve function in the brain. A small dose kills only a few nerves, the other aspects of aging kill some more nerves and eventually, if you have not died, you may become senile. I personally feel after visiting old people's homes that senility is the most tragic affliction of our age. To have to live without the hope and joy of living is to me a fate worse than death.

Epilogue: The case for the prosecution has been presented and it is not up to me to present the case for the defense. Mercury is a very useful metal and some of us will certainly suffer if we cannot enjoy the benefits of its use. Mercury has always been in our ecosphere, and some mercury in fish is not caused by man-made pollution (Goeij). Samples from museum specimens have been reported to contain as much mercury as modern tuna. I should point out that it was impractical to harvest the larger sea fish which have the high mercury levels until relatively recently.

Mercury does exist in the atmosphere from natural weathering of rocks, combustion of coal (Joensuu) and incineration of municipal and industrial wastes. Against this background the incineration of domestic sewage sludge makes a minor contribution according to our unpublished calculations. Certainly it is potentially less damaging than the same quantity of mercury dumped into rivers or leaching into streams from an unsanitary, improperly operated landfill.

Mercury also exists in the ocean, and it is hard to see how discharges of inorganic mercury could be detected if they were diluted in the whole ocean. If we could be sure that all the mercury discharges were completely mixed and not localized in coastal areas, there should be no objection. But, of course, we cannot be sure of these things.

If you ask me, "Was mercury fairly tried?" I must say "yes" based on the evidence. The fault, if any, is that we did not blow the whistle soon enough. But I agreed at the beginning not to throw stones backward in time.

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